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(54) Silica coating.

(57) A coated article having a substrate coated with a layer of silica particles is provided. The coating is substantially uniform in thickness, adheres aggressively to the substrate, and provides excellent antireflection properties to the substrate.

FIG.1

SILICA COATINGS

Background of the Invention

Field of the Invention

The present invention relates to silica coatings, articles, such as optical devices, bearing silica coatings thereon, and to processes for preparing such articles.

Background Information

Improvement in the transmittance of light through optical devices such as windows, solar collector cover plates, lenses and prisms has long been sought so as to increase their usefulness. Optical devices having surfaces coated with antireflecting layers, typically having an optical thickness of one quarter of a wavelength, are known. Also known are optical devices in which surface reflections are reduced by altering the surface to provide a gradient index of refraction between that of the medium traversed by the incident light, such as air and that of the body of the optical device.

One method for providing such an altered surface is disclosed in Great Britain Patent No. 29,561. It involves tarnishing glass surfaces in aqueous solutions of sulphuretted hydrogen in order to reduce the reflection of light therefrom. Such a method is not useful for producing an antireflection surface on polymeric substrates.

Another method for providing such an altered surface is disclosed in Nicoll (U.S. Patent No. 2,445,238). This patent discloses a method for reducing reflection from glass surfaces in which the glass is heated in a vapor of hydrofluoric acid to form a skeletonized surface. Such skeletonized surfaces are difficult to reproduce and maintain.

Moulton (U.S. Patent No. 2,432,484) discloses a technique for forming a non-gelling, nonuniformly

dispersed layer of anhydrous colloidal particles on the surface of articles. The particles form a random arrangement of peaks on the article surface to provide antireflection characteristics.

Moulton (U.S. Patent Nos. 2,536,764 and 2,601,123) discloses a transparent binder coating prepared using a dilute solution of tetraethylorthosilicate in organic solvent to render the colloidal particulate layer taught in the '484 patent resistant to wiping and handling, as such layers are inherently readily susceptable to injury.

Geffcken et al. (U.S. Patent No. 2,366,516) disclose an antireflection layer formed by applying an aqueous dispersion of a gel-like low-hydrated oxide, such as silicon dioxide, to an object and heating the coated object to a temperature of 250°C to form a hardened layer. Such a layer cannot be applied to most polymer substrates due to degradation of the substrate by heating to 250°C.

Baker et al. (U.S. Patent No. 3,301,701) disclose rendering a glass base antireflective by coating with a finely divided silica substantially free of silica gel. Such a coating would be expected to be brittle, weak, and powdery.

Land et al. (U.S. Patent No. 3,833,368) disclose antireflection coatings for photographic products which are an eighth-wave layer of a fluorinated polymer applied over an eighth-wave layer of silica, the silica layer having been formed from an aqueous colloidal silica sol.

Swerdlow (U.S. Patent No. 4,409,285) discloses an antireflection coating for optical surfaces, the coating formed from silica and/or alumina particles in a polymeric binder with particles protruding from the surface of the binder. 20 to 98 weight percent of the particles have a size in the range of 7 to 50 nanometers (nm) and 5 to 65 weight percent of

the particles have a size in the range of 75 to 150 nm.

Yoldas (U.S. Patent Nos. 4,271,210 and 4,346,131) and McCollister et al. (U.S. Patent No. 4,273,826) disclose anti-reflection coatings produced by coating a substrate with a metallo-organic compound, e.g. alkoxide, and heating the coated substrate at temperatures which decompose the organic components of the coating leaving a metal oxide layer on the substrate. The temperatures necessary to decompose the organic components would also decompose polymeric substrates.

Dorer et al. (U.S. Patent No. 4,190,321) disclose an antireflective coating of a metal oxide in the form of discrete leaflets of varying heights and shapes. This coating is susceptible to damage during handling due to the fragility of the leaflet structure.

Cathro et al, (Silica Low-Reflection Coatings for Collector Covers, by a Dip-Coating Process, SOLAR ENERGY, Vol. 32, No. 5, 1984, pp. 573-579) disclose low-reflection silica coatings prepared from ethanol-based silica sols which are aged at pH 7. Aging causes an increase in optical density and viscosity due to the agglomeration of silica particles prior to coating. Although good adhesion of the coating to glass is said to be obtained by heating at elevated temperatures, adhesion to polymeric substrates is poor, i.e., the coating can be wiped from the surface of the substrate by rubbing with a tissue.

Summary of the Invention

The present invention is directed to a coated article comprising a substrate, particularly a polymeric substrate, having a silica coating thereon. The coating comprises a continuous, gelled network

of silica particles which preferably have an average primary particle size of less than about 200A, more preferably less than about 70 A when antireflection properties are sought. The coating is substantially uniform in thickness and is substantially permanently adhered to the substrate, i.e. has a 180^{o} peelback value of at least about 150 g/cm, preferably at least about 500 g/cm.

The present invention is also directed to a process for applying coatings to substrates comprising coating a substrate with a solution containing about 0.2 to 15 weight percent colloidal silica particles, the particles preferably having an average primary particle size of less than about 200 A, and drying the coating at a temperature less than that which degrades the substrate.

The coating adheres very well to a variety of substrates, particularly polymeric substrates, and can provide such substrates with excellent average reduction in specular reflectance, e.g., at least two percent. When the substrate is transparent, the coating can provide an average increase in transmission therethrough of normal incident light in the wavelength range of 400 to 800 nm over the transmission through an uncoated substrate of the same material. The increase in transmission is preferably at least two percent and up to as much as ten percent or more. The coating can also provide antistatic properties and reduced surface resistivity to substrates, such as polymeric film and sheet materials, subject to static build-up. The coating also preferably provides abrasion resistance and slip properties to polymeric materials, such as film and sheet materials, thereby improving their handleability.

Brief Description of the Drawings

Fig. 1 is a transmission electron micrograph

of a cross section of an article of the invention;

Fig. 2 is a plot of a curve 2 of the percentage of light reflected from an uncoated polyethylene terephthalate film substrate and of a curve 3 of a coated polyethylene terephthalate film substrate according to the invention; and

Fig. 3 is a plot of a curve 4 of the percentage of light transmitted through an uncoated polyethylene terephthalate film substrate and of a curve 5 of a coated polyethylene terephthalate film substrate according to the invention.

Detailed Description of the Invention

The article of the invention is a substrate bearing a continuous gelled network of silica particles. The particles preferably have an average primary particle size of less than about 200 A. As used herein, the term "continuous" refers to covering the surface of the substrate with virtually no discontinuities or gaps in the areas where the gelled network is applied. The term "gelled network" refers to an aggregation of colloidal particles linked together to form a porous three-dimensional network. The term "porous" refers to the presence of voids between the silica particles. The term "primary particle size" refers to the average size of unagglomerated single particles of silica.

The articles of the invention comprise a substrate which may be of virtually any construction, transparent to opaque, polymeric, glass, ceramic, or metal, having a flat, curved, or complex shape and have formed thereon a continuous gelled network of silica particles. When the coating is applied to transparent substrates to achieve increased light transmissivity, the coated article preferably exhibits a total average increase in transmissivity of normal incident light of at least two percent and up to

as much as ten percent or more, depending on the substrate coated, over a range of wavelengths extending at least between 400 to 800 nm. An increase in transmissivity can also be seen at wavelengths into the infrared portion of the spectrum.

The polymeric substrates may comprise polymeric sheet, film, or molded material such as polyester, polyimide, polystyrene, polymethylmethacrylate, polycarbonate, polysulfone, polyacrylate, and cellulose acetate butyrate.

Figure 1, a transmission electron micrograph of a coating 1 useful in the invention at a magnification of 300,000X, shows that the coating is continuous, i.e., covers the surface of the substrate with virtually no discontinuities or gaps, and provides a substantially smooth surface which has only minor surface imperfections. Fig. 1 further shows that the coating 1 is substantially uniform in thickness.

The coating useful in the invention is substantially permanently adhered to substrates to which it is applied, i.e., it can provide a 180° peelback value of at least about 150 g/cm when tested according to a modification of ASTM Test Method D3330. Generally, adhesion values of 500 g/cm can be achieved with failure at the adhesive layer and no coating removal from the substrate. In the modified test method, a 1.9 cm wide strip of Scotch Brand Magic transparent tape, available from 3M Company, is adhered to the test sample by rolling a 2 kg roller back and forth twice across the tape. The tape is then peeled from the test sample at 180° at a rate of 2 cm/min.

The excellent adhesion of the coating to the substrate and the adhesive of the test tape also demonstrates the utility of the coating as a primer for adhering adhesives to substrates, such as polymeric substrates, e.g, polyester films.

The gelled network provides a porous coating having voids between the silica particles. If the open porosity is too small, the properties of the coating, such as adhesion and antireflectance may be reduced. If the open porosity is too large, the coating is weakened and may have reduced adhesion to the substrate. Generally, the colloidal solution from which the gelled network is obtained is capable of providing an open porosity of about 25 to 70 percent, preferably about 30 to 60 percent when dried. The open porosity is determined by drying a sufficient amount of the colloidal solution to provide a dried product sample of about 50 to 100 mg and analyzing the sample using a "Quantasorb" surface area analyzer available from Quantachrome Corp., Syosett, NY.

The voids of the porous coating provide a multiplicity of subwavelength interstices where the index of refraction abruptly changes from that of air to that of the coating material. These subwavelength interstices which are present throughout the coating layer, provide a coating which may have a calculated index of refraction of from about 1.15 to 1.40, preferably 1.20 to 1.30 depending on the porosity of the coating. When the porosity of the coating is high, e.g., about 70 percent, lower values for the index of refraction are obtained. When the porosity of the coating is low, e.g., 25 percent, higher values for the index of refraction are obtained. The index of refraction of the coating is dependent on the relative volume ratios of the particles and the interstices and the index of refraction of the silica, i.e., 1.47. For purposes of this invention, the index of refraction (RI) is calculated using the formula:

$$RI = \frac{P_c}{100} + \left(\frac{100-P_c}{100}\right)1.47$$

where P_o is the value of the open porosity.

The average primary particle size of the colloidal silica particles is preferably less than about 200 A to achieve good adhesion of the coating to the substrate. The average primary particle size of the colloidal silica particles is more preferably less than about 70 A when antireflection properties are sought. When the average particle size becomes too large, the resulting dried coating surface is less efficient as an antireflection coating.

The dried coating is preferably from about 20 to 500 nm thick. Such coatings provide good adhesion and antistatic properties. When the coating thickness is too great, the coating has reduced adhesion and flexibility and may flake off or form powder under mechanical stress. When antireflection properties are sought, the dried coating thickness is preferably about 70 to 250 nm, more preferably 100 to 200 nm.

Articles such as transparent sheet or film materials may be coated on a single side or on both sides to increase transmissivity, the greatest increase being achieved by coating both sides.

The process of the invention comprises coating a substrate with a solution containing about 0.2 to 15 weight percent colloidal silica particles having an average primary particle size less than about 200 A, preferably less than about 70 A, and drying the coating at a temperature less than about 200°C, preferably in the range of 80 to 120°C.

Coating may be carried out by standard coating techniques such as bar coating, roll coating, curtain coating, rotogravure coating, spraying and dipping. The substrate may be treated prior to coating to obtain a uniform coating. Various known treatment techniques include corona discharge, flame treatment, and electron beam. Generally, no pretreatment is required.

The colloidal silica solution, e.g., a hydrosol or organosol, is applied to the substrate of the article to be coated and dried at a moderately low temperature, generally less than about 200°C, preferably 80-120°C to remove water or organic diluents. The coating may also be dried at room temperature, provided the drying time is sufficient to permit the coating to dry completely. The drying temperature should be less than that at which the substrate degrades. The resulting hygroscopic coating is capable of absorbing and/or rehydrating water in an amount of up to about 15 to 20 weight percent, depending on ambient temperature and humidity conditions.

The colloidal silica solution, finely divided solid silica particles of ultramicroscopic size in a liquid, utilized in the present invention, may be acid stabilized, sodium stabilized, or ammonia stabilized. It is generally helpful to acidify sodium stabilized silica sols to a pH of about 3.5 to 4.0, e.g., with glacial acetic acid, to prevent particle agglomeration prior to preparation of the coating solution when alcohol is used as a diluent. Examples of commercially available colloidal silicas useful in the invention include Nalco 2326 and Nalco 1034A, available from Nalco Chemical Co., and Ludox LS, available from E. I. duPont de Nemours Co., Inc.

The colloidal coating solution should contain about 0.2 to 15 weight percent, preferably about 0.5 to 6 weight percent, colloidal silica particles. At particle concentrations above 15 weight percent, the resulting coating may have reduced uniformity and exhibit reduced adhesion to the substrate surface. Difficulties in obtaining a sufficiently thin coating to achieve increased light transmissivity and reduced reflection may also be encountered at concentrations above 15 weight percent. At concentrations below

0.2 weight percent, process inefficiencies result due to the large amount of solvent which must be removed and antireflection properties may be reduced.

The thickness of the applied wet coating solution is dependent on the concentration of silica particles in the coating solution and the desired thickness of the dried coating. The thickness of the wet coating solution is preferably such that the resulting dried coating thickness is from about 20 to 500 nm thick.

The coating solution may also optionally contain a surfactant to improve wettability of the solution on the substrate, but inclusion of an excessive amount of surfactant may reduce the adhesion properties of the coating. Examples of suitable surfactants include Tergitol TMN-6 (Union Carbide Corp.) and Triton X-100 (Rohm and Haas Co.). Generally, the surfactant can be used in amounts of up to about 0.5 weight percent of the solution.

The coating ingredients may optionally contain a polymeric binder. Useful polymeric binders include polyvinyl alcohol, polyvinyl acetate, polyesters, polyamides, polyvinyl pyrrolidone, copolyesters, copolymers of acrylic acid and/or methacrylic acid, and copolymers of styrene. The coating solution can contain up to about 50 weight percent of the polymeric binder based on the weight of the silica particles. Useful amounts of polymeric binder are generally in the range of 0.5 to 10.0 weight percent.

Addition of various adjuvants, such as slip agents and processing oils, to the substrate material may reduce the adhesion of the coating to the substrate.

The following specific, but non-limiting, examples will serve to illustrate the invention. In these examples, all percentages and parts are by weight unless otherwise indicated.

Example 1

Six grams of Nalco 2326 (ammonia stabilized colloidal silica; 14.5% colloidal silica as SiO_2; particle size 50A; available from Nalco Chemical Company) was added to 100 g ethanol to provide a very clear coating solution. A 0.1 mm biaxially oriented polyethylene terephthalate film containing an ultraviolet absorber was dipped in the coating solution, air dryed, and dried at 100°C for two minutes. The resulting coating was porous, continuous, and similar to the coating shown in Fig. 1 in appearance. The coating thickness was about 120 nm.

The coating adhered aggressively to the substrate. A 3/4 inch wide strip of Scotch Brand Magic transparent tape was applied to coated and uncoated film samples by hand pressure. A force of about 180 g/cm tape width was required to remove the tape from the uncoated sample, while a force of about 530 g/cm tape width was required to remove the tape from the coated sample, demonstrating a remarkable increase in the adhesion of the tape. The adhesive of the tape did not remove the coating from the coated film, but exhibited adhesive split of the adhesive layer leaving adhesive residue on the coating further demonstrating the strong bond of the adhesive to the coated film. No adhesive split was observed when the tape was removed from the uncoated sample.

The antireflection and transmission properties of the film were measured using an IBM UV-VIS 9432 Spectrophotometer at wavelengths of from 350 to 800 nm. An uncoated sample of the film was also measured for comparative purposes. The results of these tests are shown in Figs. 2 and 3. As can be seen from Fig. 2, the reflectance of the uncoated sample, curve 2, was about 12% at 600 nm, while the reflectance

of the coated sample, curve 3, was about 2% at 600 nm. As can be seen from Fig. 3, the light transmission of the uncoated film, curve 4, was about 88% at 600 nm, while the light transmission of the coated sample, curve 5, was about 98% at 600 nm. This demonstrates the excellent reduction of reflectance and increase in transmission of light provided by the coating.

Example 2

A coating solution was prepared by diluting colloidal silica (Nalco 2326) with ethanol to a concentration of 2.5% solids and adding 0.01% Tergitol TMN-6. The solution was coated on 0.1 mm thick polyethylene terephthalate film using a rotogravure coating roll. The coated film was dried at 93°C for three minutes. The resulting coating was porous, continuous, and about 100 nm thick. The coating was substantially similar to the coating shown in Fig. 1. The dried coating was observed to have good antireflection properties.

Samples of the coated film as well as samples of uncoated film were tested for adhesion using the modified ASTM Test Method D3330 described hereinabove. The uncoated film had an adhesion value of 189 g/cm tape width with no adhesive split from the tape. The coated sample had an adhesion value of 559 g/cm tape width. The tape did not remove the coating from the film, but exhibited adhesive split of the adhesive layer, again demonstrating the excellent adhesion of the coating to the substrate and the excellent adhesion of the adhesive to the coating.

Examples 3-15

Various transparent polymeric sheet materials, as identified in Table 1, were coated by dipping the materials in a coating solution containing 1.5% colloidal silica (Nalco 2326) or by wiping the solution

on each side of the sheet material with a tissue-wrapped glass rod and drying the coated sample.

Table 1

Material	Type	Thickness (mm)
A	polymethylmethacrylate (Rohm and Haas Co.)	0.67
B	polycarbonate (CR-39, PPG Inc.)	3.12
C	polycarbonate (Lexan, General Electric Co.)	1.94
D	cellulose acetate butyrate	2.15

The following coating solutions were used to coat the various sheet materials:

Solution I

ethanol	135 g
Nalco 2326 silica sol	15 g
Tergitol TMN-6	0.15 g

Solution II

water	135 g
Nalco 2326 silica sol	15 g
Tergitol TMN-6	0.3 g

For each example, the substrate material, coating method, coating solution, and drying temperature, together with the resulting light transmission determined using an IBM UV-VIS 9432 Spectrophotometer at wavelengths of from 400 to 800 nm, are set forth in Table 2. Light transmission data for uncoated materials are also set forth in Table 2 for comparative purposes.

Table 2

Example	Material	Coating Method	Coating Solution	Drying Temp. (°C)	% Transmission at wavelengths (nm) 400	500	600	700	800	Average percent increase in transmission
3 (Comp)*	A	none	---	---	92.0	92.5	92.5	92.5	92.5	---
4	A	dip	I	80	91.5	93.5	94.5	95.5	95.5	2.0
5	A	wipe	I	80	96.5	94.8	94.7	95.3	95.6	3.2
6 (Comp)	B	none	---	---	88.5	90.5	91.0	91.4	91.8	---
7	B	wipe	II	22	96.0	97.5	97.5	97.0	96.0	6.8
8	B	wipe	II	80	92.1	94.2	96.0	97.1	97.5	5.2
9	B	wipe	I	22	93.0	96.0	97.4	97.9	97.5	6.3
10	B	wipe	I	80	91.8	94.5	97.0	98.0	98.2	5.8
11 (Comp)	C	none	---	---	91.7	92.0	92.0	92.1	92.1	---
12	C	wipe	I	80	94.1	92.6	94.1	96.2	98.0	3.3
13 (Comp)	D	none	---	---	83.6	87.9	87.5	90.1	90.2	---
14	D	dip	II	22	87.1	93.8	93.7	96.2	96.1	6.3
15	D	wipe	I	80	86.0	90.4	89.1	91.8	92.8	2.5

*"Comp" denotes comparative examples.

As can be seen from the data in Table 2, the coatings provide an excellent increase in light transmission for each of the materials which were coated. Each coated sample exhibited at least two percent average increase in light transmission. The greatest increase in transmission was achieved on the CR-39 polycarbonate with the average percent increase in transmission for Example 7 being 6.8 percent.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

CLAIMS:

1. A coated article comprising a substrate having a coating of a continuous, gelled network of silica particles which coating is substantially uniform in thickness and is substantially permanently adhered to said substrate.

2. The coated article of claim 1 wherein said silica particles have a primary particle size of less than about 200 A.

3. The coated article of claim 1 wherein said coating provides a 180° peelback value of at least about 150 g/cm.

4. The coated article of claim 1 wherein said coating is about 20 to 500 nm thick.

5. The coated article of claim 1 wherein said coating is prepared from a colloidal solution capable of providing a dried product having an open porosity of between about 25 and 70 percent.

6. The coated article of claim 1 wherein said coating contains up to about 20 weight percent water.

7. The coated article of claim 1 wherein said substrate is transparent.

8. The coated article of claim 7 wherein the transmission therethrough of normal incident light in the wavelength range of 400 to 800 nm is increased over the transmission through an uncoated substrate of the same composition.

9. The coated article of claim 8 wherein said average transmission is increased at least 2 percent.

10. The coated article of claim 8 wherein said coating is from about 70 to 250 nm thick.

11. The coated article of claim 8 wherein said coating has an index of refraction of between about 1.15 and 1.40.

12. The coated article of claim 1 or 7 wherein said substrate is polymeric.

13. The process for forming coated article of claim 1 comprising coating said substrate with a solution containing colloidal silica particles, and drying said coating at a temperature less than that which degrades said substrate to form a substantially continuous, gelled network of silica particles which is substantially uniform in thickness and is substantially permanently adhered to said substrate.

14. The process of claim 13 wherein said particles have an average primary particle size of less than about 200 A.

15. The process of claim 13 wherein the coating is dried at a temperature of less than 200°C.

16. The process of claim 13 wherein the coating is dried at a temperature in the range of 80°C to 120°C.

FIG.1

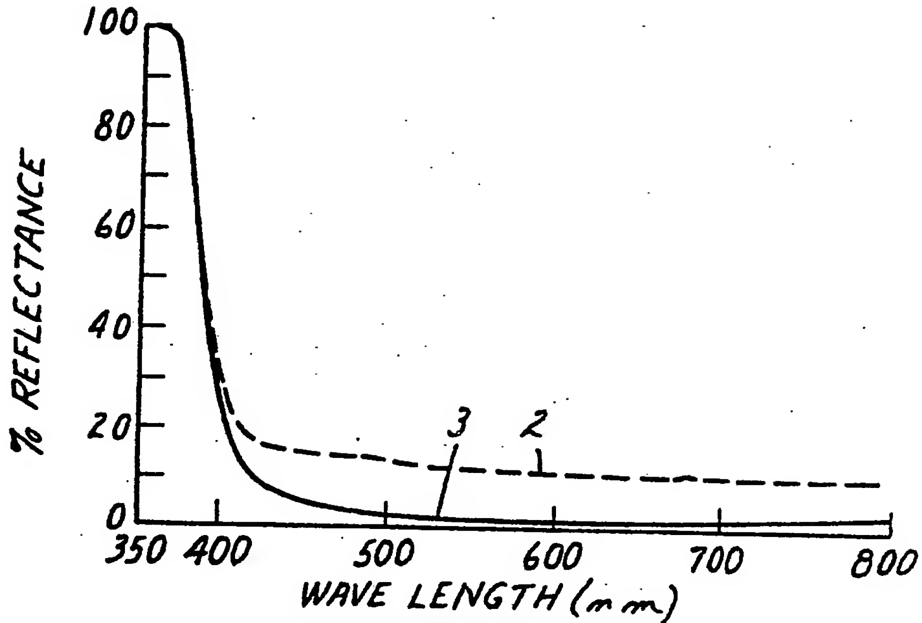
100
80
60
40
20
0
% REFLECTANCE
350
400
500
600
700
800
WAVE LENGTH (nm)
3
2

FIG. 2

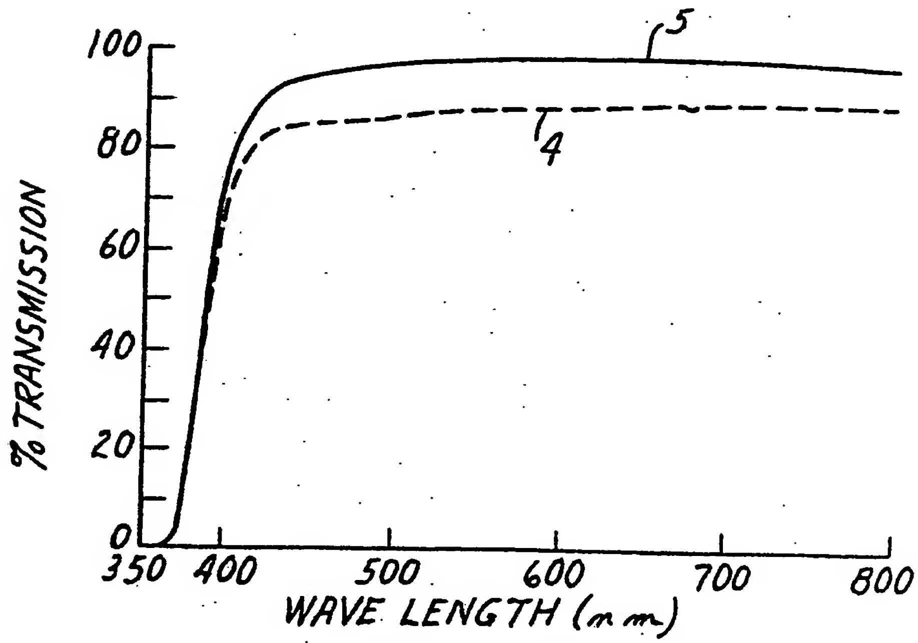
100
80
60
40
20
0
% TRANSMISSION
350
400
500
600
700
800
WAVE LENGTH (nm)
5
4

FIG. 3

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(54) **Silica coating.**

(57) A coated article having a substrate coated with a layer of silica particles is provided. The coating is substantially uniform in thickness, adheres aggressively to the substrate, and provides excellent antireflection properties to the substrate.

FIG.1

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0193269

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EUROPEAN SEARCH REPORT

Application Number

EP 86 30 0424

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	PATENT ABSTRACTS OF JAPAN, vol. 7, no. 238 (P-231)[1383], 22nd October 1983; & JP-A-58 126 502 (NIHON ITA GLASS K.K.) 28-07-1983 * Abstract *	1-16	C 09 D 3/82 G 02 B 1/10
X	US-A-4 271 210 (B.Y.YOLPAS) * Claim 1; column 2, lines 43-54 *	1	
P,Y	US-A-2 536 764 (H.R.MOULTON) * Claims 1-5; column 3, lines 11-70 *	1	
D,Y	US-A-2 601 123 (H.R.MOULTON) * Claims 1-12; column 3, lines 2-75 *	1	
D,Y	US-A-4 409 285 (M.S.SWERDLOW) * Claim 1; column 1, lines 37-55 *	1	
Y	EP-A-0 130 801 (WESTINGHOUSE) * Claims 1,8; page 1, lines 1-7 *	1	
A	EP-A-3 986 997 (H.A.CLARK) * Claim 1; column 4, lines 29-60 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	US-A-3 707 751 (R.D.MISCH) * Claims 1,3; column 8, lines 32-68; column 9, lines 1-18; column 12, lines 60-67; column 13, lines 1-11 *	1	C 09 D G 02 B B 29 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14-12-1988	DEPIJPER R.D.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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US-A- 3 707 751
US-A- 4 409 285
EP-A- 3 986 997
US-A- 2 601 123
US-A- 4 271 210

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Description

The present invention relates to silica coatings, articles, such as optical devices, bearing silica coatings thereon, and to processes for preparing such articles.

Improvement in the transmittance of light through optical devices such as windows, solar collector cover plates, lenses and prisms has long been sought so as to increase their usefulness. Optical devices having surfaces coated with antireflecting layers, typically having an optical thickness of one quarter of a wavelength, are known. Also known are optical devices in which surface reflections are reduced by altering the surface to provide a gradient index of refraction between that of the medium traversed by the incident light, such as air and that of the body of the optical device.

One method for providing such an altered surface is disclosed in Great Britain Patent No. 29,561. It involves tarnishing glass surfaces in aqueous solutions of sulphuretted hydrogen in order to reduce the reflection of light therefrom. Such a method is not useful for producing an antireflection surface on polymeric substrates.

Another method for providing such an altered surface is disclosed in Nicoll (U.S. Patent No. 2,445,238). This patent discloses a method for reducing reflection from glass surfaces in which the glass is heated in a vapor of hydrofluoric acid to form a skeletonized surface. Such skeletonized surfaces are difficult to reproduce and maintain.

Moulton (U.S. Patent No. 2,432,484) discloses a technique for forming a non-gelling, nonuniformly dispersed layer of anhydrous colloidal particles on the surface of articles. The particles form a random arrangement of peaks on the article surface to provide antireflection characteristics.

Moulton (U.S. Patent Nos. 2,536,764 and 2,601,123) discloses a transparent binder coating prepared using a dilute solution of tetraethylorthosilicate in organic solvent to render the colloidal particulate layer taught in the '484 patent resistant to wiping and handling, as such layers are inherently readily susceptable to injury.

Geffcken et al. (U.S. Patent No. 2,366,516) disclose an antireflection layer formed by applying an aqueous dispersion of a gel-like low-hydrated oxide, such as silicon dioxide, to an object and heating the coated object to a temperature of 250°C to form a hardened layer. Such a layer cannot be applied to most polymer substrates due to degradation of the substrate by heating to 250°C.

Baker et al. (U.S. Patent No. 3,301,701) disclose rendering a glass base antireflective by coating with a finely divided silica substantially free of silica gel. Such a coating would be expected to be brittle, weak, and powdery.

Land et al. (U.S. Patent No. 3,833,368) disclose antireflection coatings for photographic products which are an eighth-wave layer of a fluorinated polymer applied over an eighth-wave layer of silica, the silica layer having been formed from an aqueous colloidal silica sol.

Swerdlow (U.S. Patent No. 4,409,285) discloses an antireflection coating for optical surfaces, the coating formed from silica and/or alumina particles in a polymeric binder with particles protruding from the surface of the binder. 20 to 98 weight percent of the particles have a size in the range of 7 to 50 nanometers (nm) and 5 to 65 weight percent of the particles have a size in the range of 75 to 150 nm.

Yoldas (U.S. Patent Nos. 4,271,210 and 4,346,131) and McCollister et al. (U.S. Patent No. 4,273,826) disclose anti-reflection coatings produced by coating a substrate with a metallo-organic compound, e.g. alkoxide, and heating the coated substrate at temperatures which decompose the organic components of the coating leaving a metal oxide layer on the substrate. The temperatures necessary to decompose the organic components would also decompose polymeric substrates.

Dorer et al. (U.S. Patent No. 4,190,321) disclose an antireflective coating of a metal oxide in the form of discrete leaflets of varying heights and shapes. This coating is susceptible to damage during handling due to the fragility of the leaflet structure.

Cathro et al, (Silica Low-Reflection Coatings for Collector Covers, by a Dip-Coating Process, SOLAR ENERGY, Vol. 32, No. 5, 1984, pp. 573-579) disclose low-reflection silica coatings prepared from ethanol-based silica sols which are aged at pH 7. Aging causes an increase in optical density and viscosity due to the agglomeration of silica particles prior to coating. Although good adhesion of the coating to glass is said to be obtained by heating at elevated temperatures, adhesion to polymeric substrates is poor, i.e., the coating can be wiped from the surface of the substrate by rubbing with a tissue.

Summary of the Invention

The present invention is directed to a process for forming a coated article comprising coating a substrate with a solution containing 0.2 to 15 weight percent colloidal silica particles having an average

primary particle size of less than 20 nm (200A), and drying said coating at a temperature of less than 200 °C to form a substrate having a coating of a continuous gelled network of silica particles which is transparent, provides a substantially smooth surface, is substantially uniform in thickness and is substantially permanently adhered to said substrate providing a 180° peelback value of at least 500 g/cm.

The present invention is also directed to a coated article prepared according to this method.

The coating adheres very well to a variety of substrates, particularly polymeric substrates, and can provide such substrates with excellent average reduction in specular reflectance, e.g., at least two percent. When the substrate is transparent, the coating can provide an average increase in transmission therethrough of normal incident light in the wavelength range of 400 to 800 nm over the transmission through an uncoated substrate of the same material. The increase in transmission is preferably at least two percent and up to as much as ten percent or more. The coating can also provide antistatic properties and reduced surface resistivity to substrates, such as polymeric film and sheet materials, subject to static build-up. The coating also preferably provides abrasion resistance and slip properties to polymeric materials, such as film and sheet materials, thereby improving their handleability.

Brief Description of the Drawings

Fig. 1 is a transmission electron micrograph of a cross section of an article of the invention;

Fig. 2 is a plot of a curve 2 of the percentage of light reflected from an uncoated polyethylene terephthalate film substrate and of a curve 3 of a coated polyethylene terephthalate film substrate according to the invention; and

Fig. 3 is a plot of a curve 4 of the percentage of light transmitted through an uncoated polyethylene terephthalate film substrate and of a curve 5 of a coated polyethylene terephthalate film substrate according to the invention.

Detailed Description of the Invention

The article of the invention is a substrate bearing a continuous gelled network of silica particles. The particles preferably have an average primary particle size of less than about 20 nm (200 A). As used herein, the term "continuous" refers to covering the surface of the substrate with virtually no discontinuities or gaps in the areas where the gelled network is applied. The term "gelled network" refers to an aggregation of colloidal particles linked together to form a porous three-dimensional network. The term "porous" refers to the presence of voids between the silica particles. The term "primary particle size" refers to the average size of unagglomerated single particles of silica.

The articles of the invention comprise a substrate which may be of virtually any construction, transparent to opaque, polymeric, glass, ceramic, or metal, having a flat, curved, or complex shape and have formed thereon a continuous gelled network of silica particles. When the coating is applied to transparent substrates to achieve increased light transmissivity, the coated article preferably exhibits a total average increase in transmissivity of normal incident light of at least two percent and up to as much as ten percent or more, depending on the substrate coated, over a range of wavelengths extending at least between 400 to 800 nm. An increase in transmissivity can also be seen at wavelengths into the infrared portion of the spectrum.

The polymeric substrates may comprise polymeric sheet, film, or molded material such as polyester, polyimide, polystyrene, polymethylmethacrylate, polycarbonate, polysulfone, polyacrylate, and cellulose acetate butyrate.

Figure 1, a transmission electron micrograph of a coating 1 useful in the invention at a magnification of 300,000X, shows that the coating is continuous, i.e., covers the surface of the substrate with virtually no discontinuities or gaps, and provides a substantially smooth surface which has only minor surface imperfections. Fig. 1 further shows that the coating 1 is substantially uniform in thickness.

The coating useful in the invention is substantially permanently adhered to substrates to which it is applied, i.e., it can provide a 180° peelback value of at least about 500 g/cm when tested according to a modification of ASTM Test Method D3330, generally with failure at the adhesive layer and no coating removal from the substrate. In the modified test method, a 1.9 cm wide strip of Scotch Brand Magic transparent tape, available from 3M Company, is adhered to the test sample by rolling a 2 kg roller back and forth twice across the tape. The tape is then peeled from the test sample at 180° at a rate of 2 cm/min.

The excellent adhesion of the coating to the substrate and the adhesive of the test tape also demonstrates the utility of the coating as a primer for adhering adhesives to substrates, such as polymeric substrates, e.g, polyester films.

The gelled network provides a porous coating having voids between the silica particles. If the open porosity is too small, the properties of the coating, such as adhesion and antireflectance may be reduced. If the open porosity is too large, the coating is weakened and may have reduced adhesion to the substrate. Generally, the colloidal solution from which the gelled network is obtained is capable of providing an open porosity of 25 to 70 percent, preferably 30 to 60 percent when dried. The open porosity is determined by drying a sufficient amount of the colloidal solution to provide a dried product sample of about 50 to 100 mg and analyzing the sample using a "Quantasorb" surface area analyzer available from Quantachrome Corp., Syosett, NY.

The voids of the porous coating provide a multiplicity of subwavelength interstices where the index of refraction abruptly changes from that of air to that of the coating material. These subwavelength interstices which are present throughout the coating layer, provide a coating which may have a calculated index of refraction of from 1.15 to 1.40, preferably 1.20 to 1.30 depending on the porosity of the coating. When the porosity of the coating is high, e.g., about 70 percent, lower values for the index of refraction are obtained. When the porosity of the coating is low, e.g., 25 percent, higher values for the index of refraction are obtained. The index of refraction of the coating is dependent on the relative volume ratios of the particles and the interstices and the index of refraction of the silica, i.e., 1.47. For purposes of this invention, the index of refraction (RI) is calculated using the formula:

$$RI = \frac{P_o}{100} + \left(\frac{100-P_c}{100}\right)1.47$$

where Po is the value of the open porosity.

The average primary particle size of the colloidal silica particles is preferably less than about 20 nm (200 A) to achieve good adhesion of the coating to the substrate. The average primary particle size of the colloidal silica particles is more preferably less than about 7nm (70 A) when antireflection properties are sought. When the average particle size becomes too large, the resulting dried coating surface is less efficient as an antireflection coating.

The dried coating is preferably from about 20 to 500 nm thick. Such coatings provide good adhesion and antistatic properties. When the coating thickness is too great, the coating has reduced adhesion and flexibility and may flake off or form powder under mechanical stress. When antireflection properties are sought, the dried coating thickness is preferably about 70 to 250 nm, more preferably 100 to 200 nm.

Articles such as transparent sheet or film materials may be coated on a single side or on both sides to increase transmissivity, the greatest increase being achieved by coating both sides.

The process of the invention comprises coating a substrate with a solution containing about 0.2 to 15 weight percent colloidal silica particles having an average primary particle size less than about 20 nm (200 A), Preferably less than about 7 nm (70 A). and drying the coating at a temperature less than 200°C, preferably in the range of 80 to 120°C.

Coating may be carried out by standard coating techniques such as bar coating, roll coating, curtain coating, rotogravure coating, spraying and dipping. The substrate may be treated prior to coating to obtain a uniform coating. Various known treatment techniques include corona discharge, flame treatment, and electron beam. Generally, no pretreatment is required.

The colloidal silica solution, e.g., a hydrosol or organosol, is applied to the substrate of the article to be coated and dried at a temperature, less than about 200°C, preferably 80-120°C to remove water or organic diluents. The coating may also be dried at room temperature, provided the drying time is sufficient to permit the coating to dry completely. The drying temperature should be less than that at which the substrate degrades. The resulting hygroscopic coating is capable of absorbing and/or rehydrating water in an amount of up to about 15 to 20 weight percent, depending on ambient temperature and humidity conditions.

The colloidal silica solution, finely divided solid silica particles of ultramicroscopic size in a liquid, utilized in the present invention, may be acid stabilized, sodium stabilized, or ammonia stabilized. It is generally helpful to acidify sodium stabilized silica sols to a pH of 3.5 to 4.0, e.g., with glacial acetic acid, to prevent particle agglomeration prior to preparation of the coating solution when alcohol is used as a diluent. Examples of commercially available colloidal silicas useful in the invention include Nalco 2326 and Nalco 1034A, available from Nalco Chemical Co., and Ludox LS, available from E. I. duPont de Nemours Co., Inc.

The colloidal coating solution should contain 0.2 to 15 weight percent, preferably about 0.5 to 6 weight percent, colloidal silica particles. At particle concentrations above 15 weight percent, the resulting coating

may have reduced uniformity and exhibit reduced adhesion to the substrate surface. Difficulties in obtaining a sufficiently thin coating to achieve increased light transmissivity and reduced reflection may also be encountered at concentrations above 15 weight percent. At concentrations below 0.2 weight percent, process inefficiencies result due to the large amount of solvent which must be removed and antireflection properties may be reduced.

The thickness of the applied wet coating solution is dependent on the concentration of silica particles in the coating solution and the desired thickness of the dried coating. The thickness of the wet coating solution is preferably such that the resulting dried coating thickness is from 20 to 500 nm thick.

The coating solution may also optionally contain a surfactant to improve wettability of the solution on the substrate, but inclusion of an excessive amount of surfactant may reduce the adhesion properties of the coating. Examples of suitable surfactants include Tergitol TMN-6 (Union Carbide Corp.) and Triton X-100 (Rohm and Haas Co.). Generally, the surfactant can be used in amounts of up to about 0.5 weight percent of the solution.

The coating ingredients may optionally contain a polymeric binder. Useful polymeric binders include polyvinyl alcohol, polyvinyl acetate, polyesters, polyamides, polyvinyl pyrrolidone, copolyesters, copolymers of acrylic acid and/or methacrylic acid, and copolymers of styrene. The coating solution can contain up to about 50 weight percent of the polymeric binder based on the weight of the silica particles. Useful amounts of polymeric binder are generally in the range of 0.5 to 10.0 weight percent.

Addition of various adjuvants, such as slip agents and processing oils, to the substrate material may reduce the adhesion of the coating to the substrate.

The following specific, examples will serve to illustrate the invention. In these examples, all percentages and parts are by weight unless otherwise indicated.

Example 1

Six grams of Nalco 2326 (ammonia stabilized colloidal silica; 14.5% colloidal silica as SiO_2; particle size 5 nm (50 A); available form Nalco Chemical Company) was added to 100 g ethanol to provide a very clear coating solution. A 0.1 mm biaxially oriented polyethylene terephthalate film containing an ultraviolet absorber was dipped in the coating solution, air dryed, and dried at 100°C for two minutes. The resulting coating was porous, continuous, and similar to the coating shown in Fig. 1 in appearance. The coating thickness was about 120 nm.

The coating adhered aggressively to the substrate. A 1.9 cm (3/4 inch) wide strip of Scotch Brand Magic transparent tape was applied to coated and uncoated film samples by hand pressure. A force of about 180 g/cm tape width was required to remove the tape from the uncoated sample, while a force of about 530 g/cm tape width was required to remove the tape from the coated sample, demonstrating a remarkable increase in the adhesion of the tape. The adhesive of the tape did not remove the coating from the coated film, but exhibited adhesive split of the adhesive layer leaving adhesive residue on the coating further demonstrating the strong bond of the adhesive to the coated film. No adhesive split was observed when the tape was removed from the uncoated sample.

The antireflection and transmission properties of the film were measured using an IBM UV-VIS 9432 Spectrophotometer at wavelengths of from 350 to 800 nm. An uncoated sample of the film was also measured for comparative purposes. The results of these tests are shown in Figs. 2 and 3. As can be seen from Fig. 2, the reflectance of the uncoated sample, curve 2, was 12% at 600 nm, while the reflectance of the coated sample, curve 3, was about 2% at 600 nm. As can be seen from Fig. 3, the light transmission of the uncoated film, curve 4, was about 88% at 600 nm, while the light transmission of the coated sample, curve 5, was about 98% at 600 nm. This demonstrates the excellent reduction of reflectance and increase in transmission of light provided by the coating.

Example 2

A coating solution was prepared by diluting colloidal silica (Nalco 2326) with ethanol to a concentration of 2.5% solids and adding 0.01% Tergitol TMN-6. The solution was coated on 0.1 mm thick polyethylene terephthalate film using a rotogravure coating roll. The coated film was dried at 93°C for three minutes. The resulting coating was porous, continuous, and about 100 nm thick. The coating was substantially similar to the coating shown in Fig. 1. The dried coating was observed to have good antireflection properties.

Samples of the coated film as well as samples of uncoated film were tested for adhesion using the modified ASTM Test Method D3330 described hereinabove. The uncoated film had an adhesion value of 189 g/cm tape width with no adhesive split from the tape. The coated sample had an adhesion value of 559

g/cm tape width. The tape did not remove the coating from the film, but exhibited adhesive split of the adhesive layer, again demonstrating the excellent adhesion of the coating to the substrate and the excellent adhesion of the adhesive to the coating.

Examples 3-15

Various transparent polymeric sheet materials, as identified in Table 1, were coated by dipping the materials in a coating solution containing 1.5% colloidal silica (Nalco 2326) or by wiping the solution on each side of the sheet material with a tissue-wrapped glass rod and drying the coated sample.

Table 1

Material	Type	Thickness (mm)
A	polymethylmethacrylate (Rohm and Haas Co.)	0.67
B	polycarbonate (CR-39, PPG Inc.)	3.12
C	polycarbonate (Lexan, General Electric Co.)	1.94
D	cellulose acetate butyrate	2.15

The following coating solutions were used to coat the various sheet materials:

Solution I	
ethanol	135 g
Nalco 2326 silica sol	15 g
Tergitol TMN-6	0.15 g

Solution II	
water	135 g
Nalco 2326 silica sol	15 g
Tergitol TMN-6	0.3 g

For each example, the substrate material, coating method, coating solution, and drying temperature, together with the resulting light transmission determined using an IBM UV-VIS 9432 Spectrophotometer at wavelengths of from 400 to 800 nm, are set forth in Table 2. Light transmission data for uncoated materials are also set forth in Table 2 for comparative purposes.

Table 2

Example	Material	Coating Method	Coating Solution	Drying Temp. (°C)	% Transmission at wavelengths (nm) 400	500	600	700	800	Average percent increase in transmission
3 (Comp)*	A	none	---	---	92.0	92.5	92.5	92.5	92.5	---
4	A	dip	I	80	91.5	93.5	94.5	95.5	95.5	2.0
5	A	wipe	I	80	96.5	94.8	94.7	95.3	95.6	3.2
6 (Comp)	B	none	---	---	88.5	90.5	91.0	91.4	91.8	---
7	B	wipe	II	22	96.0	97.5	97.5	97.0	96.0	6.8
8	B	wipe	II	80	92.1	94.2	96.0	97.1	97.5	5.2
9	B	wipe	I	22	93.0	96.0	97.4	97.9	97.5	6.3
10	B	wipe	I	80	91.8	94.5	97.0	98.0	98.2	5.8
11 (Comp)	C	none	---	---	91.7	92.0	92.0	92.1	92.1	---
12	C	wipe	I	80	94.1	92.6	94.1	96.2	98.0	3.3
13 (Comp)	D	none	---	---	83.6	87.9	87.5	90.1	90.2	---
14	D	dip	II	22	87.1	93.8	93.7	96.2	96.1	6.3
15	D	wipe	I	80	86.0	90.4	89.1	91.8	92.8	2.5

*"Comp" denotes comparative examples.

As can be seen from the data in Table 2, the coatings provide an excellent increase in light transmission for each of the materials which were coated. Each coated sample exhibited at least two percent average increase in light transmission. The greatest increase in transmission was achieved on the CR-39 polycarbonate with the average percent increase in transmission for Example 7 being 6.8 percent.

Claims

1. A process for forming a coated article comprising coating a substrate with a solution containing 0.2 to 15 weight percent colloidal silica particles having an average primary particle size of less than 20 nm (200A), and drying said coating at a temperature of less than 200 °C to form a substrate having a coating of a continuous gelled network of silica particles which is transparent, provides a substantially smooth surface, is substantially uniform in thickness and is substantially permanently adhered to said substrate providing a 180° peelback value of at least 500 g/cm.

2. The process of claim 1 wherein the coating is dried at a temperature in the range of 80 °C to 120 °C.

3. The process of any preceding claim wherein said coating is 20 to 500 nm thick.

4. The process of any preceding claim wherein said coating is prepared from a colloidal solution capable of providing a dried product having an open porosity of between 25 and 70 percent.

5. The process of any preceding claim wherein said coating contains up to about 20 weight percent water.

6. The process of any preceding claim wherein said substrate is transparent.

7. The process of claim 6 wherein the transmission therethrough of normal incident light in the wavelength range of 400 to 800 nm is increased over the transmission through an uncoated substrate of the same compositions.

8. The process of claim 7 wherein said average transmission is increased at least 2 percent.

9. The process of either of claims 7 and 8 wherein said coating is from about 70 to 250 nm thick.

10. The process of any preceding claim wherein said coating has an index of refraction of between 1.15 and 1.40.

11. The process of any preceding claim wherein said substrate is polymeric.

12. A coated article prepared according to the method of any preceding claim.

Patentansprüche

1. Verfahren zur Erzeugung eines beschichteten Gegenstands, umfassend Beschichten eines Substrats mit einer Lösung, die 0,2 bis 15 Gewichtsprozent kolloidale Silicateilchen mit einer mittleren Primärteilchengröße von weniger als 20 nm (200 Å) enthält, und Trocknen der Beschichtung bei einer Temperatur von weniger als 200 °C, um ein Substrat mit einer Beschichtung eines zusammenhängenden, durch Gelbildung erstarrten Netzwerks von Silicateilchen zu erzeugen, die transparent ist, eine im wesentlichen glatte Oberfläche schafft, eine im wesentlichen gleichförmige Dicke aufweist und im wesentlichen dauerhaft auf dem Substrat haftet und einen 180°-Ablösewert von mindestens 500 g/cm gewährt.

2. Verfahren nach Anspruch 1, bei welchem die Beschichtung bei einer Temperatur im Bereich von 80 °C bis 120 °C getrocknet wird.

3. Verfahren nach einem der vorstehenden Ansprüche, bei welchem die Beschichtung 20 bis 500 nm dick ist.

4. Verfahren nach einem der vorstehenden Ansprüche, bei welchem die Beschichtung aus einer kolloidalen Lösung hergestellt wird, mit der ein getrocknetes Produkt mit einer offenen Porosität zwischen 25 und 70 Prozent geschaffen werden kann.

5. Verfahren nach einem vorstehenden Ansprüche, bei welchem die Beschichtung bis zu etwa 20 Gewichtsprozent Wasser enthält.

6. Verfahren nach einem der vorstehenden Ansprüche, bei welchem das Substrat transparent ist.

7. Verfahren nach Anspruch 6, bei welchem die Durchlässigkeit bei senkrecht einfallendem Licht im Wellenlängenbereich zwischen 400 und 800 nm gegenüber der Durchlässigkeit durch ein unbeschichtetes Substrat der gleichen Zusammensetzungen erhöht ist.

8. Verfahren nach Anspruch 7, bei welchem die mittlere Durchlässigkeit um mindestens 2 Prozent erhöht ist.

9. Verfahren nach Anspruch 7 oder 8, bei welchem die Beschichtung zwischen 70 und 250 nm dick ist.

10. Verfahren nach einem vorstehenden Ansprüche, bei welchem die Beschichtung einen Brechungsindex zwischen 1,15 und 1,40 hat.

11. Verfahren nach einem der vorstehenden Ansprüche, bei welchem das Substrat ein Polymer ist.

12. Beschichteter Gegenstand, der gemäß dem Verfahren nach einem der vorstehenden Ansprüche hergestellt wird.

Revendications

1. Procédé de formation d'un article revêtu, comprenant l'application en couche sur un substrat d'une solution contenant 0,2 à 15 % en poids de particules de silice colloïdale, ayant une taille primaire moyenne des particules de moins de 20 nm (200 A), et le séchage de ce revêtement à une température inférieure à 200 °C pour former un substrat comportant un revêtement d'un réseau gélifié continu de particules de silice, qui est transparent, donne une surface essentiellement lisse, est d'une épaisseur pratiquement uniforme et est amené à adhérer de manière pratiquement permanente au substrat susdit, en donnant une valeur de pelage à 180° d'au moins 500 g/cm.

2. Procédé suivant la revendication 1, dans lequel le revêtement est séché à une température de l'ordre de 80 à 120 °C.

3. Procédé suivant l'une quelconque des revendications précédentes, dans lequel ce revêtement a une épaisseur de 20 à 500 nm.

4. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le revêtement est préparé au départ d'une solution colloïdale capable de donner un produit séché ayant une porosité ouverte comprise entre 25 et 70 %.

5. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le revêtement susdit contient jusqu'à environ 20 % en poids d'eau.

6. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le substrat précité est transparent.

7. Procédé suivant la revendication 6, dans lequel la transmission, à travers ce substrat, d'une lumière incidente normale dans l'intervalle de longueurs d'onde de 400 à 800 nm est accrue par rapport à la transmission à travers un substrat non revêtu, de la même composition.

8. Procédé suivant la revendication 7, dans lequel la transmission moyenne susdite est augmentée d'au moins 2 %.

9. Procédé suivant la revendication 7 ou la revendication 8, dans lequel le revêtement précité est d'une épaisseur d'environ 70 à 250 nm.

10. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le revêtement précité a un indice de réfraction compris entre 1,15 et 1,40.

11. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le substrat précité est un substrat polymérique.

12. Article revêtu, préparé suivant le procédé de l'une quelconque des revendications précédentes.

FIG.1

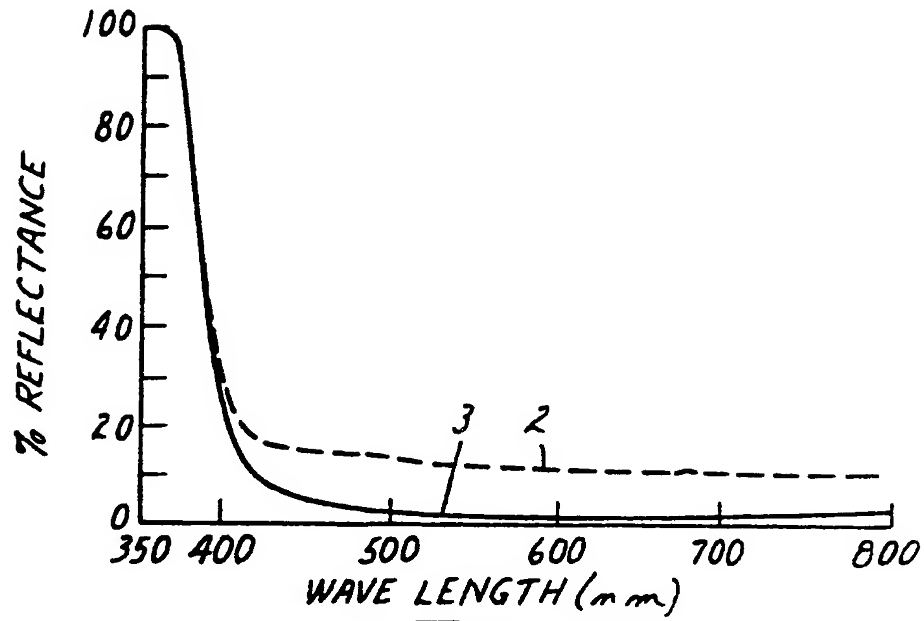
100
80
60
40
20
0
% REFLECTANCE
3
2
350
400
500
600
700
800
WAVE LENGTH (nm)

FIG. 2

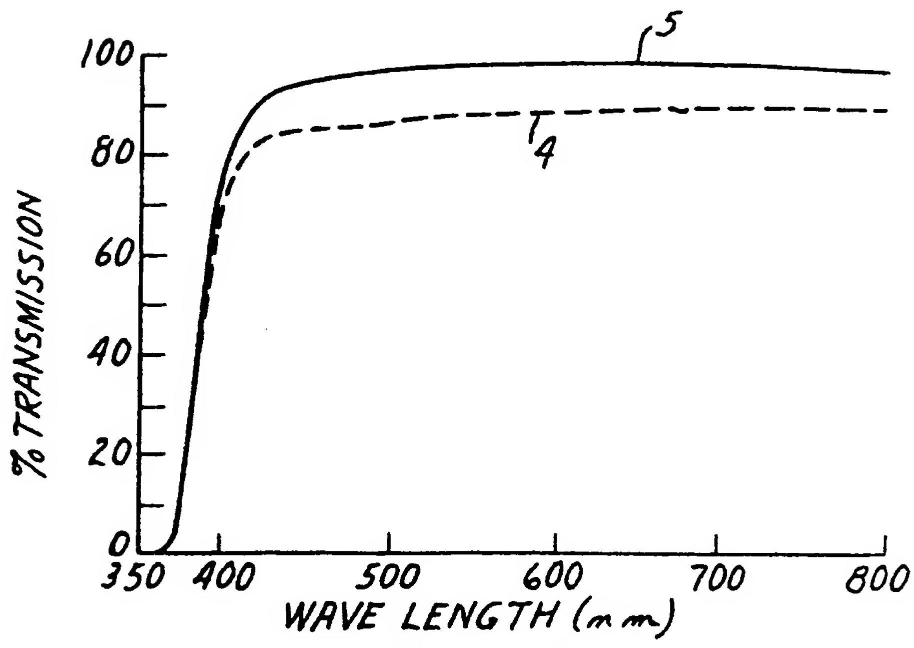
5
100
80
60
40
20
0
% TRANSMISSION
4
350
400
500
600
700
800
WAVE LENGTH (nm)

FIG. 3

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(54) **Silica coating**

Beschichtungszusammensetzung auf Basis von Silica

Composition de revêtement à base de silice

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US-A- 2 536 764
US-A- 2 601 123
US-A- 3 707 751
US-A- 3 986 997
US-A- 4 191 804
US-A- 4 271 210
US-A- 4 310 600
US-A- 4 390 373
US-A- 4 409 285
US-A- 4 446 171
US-A- 4 478 873
US-A- 4 584 280

- **PATENT ABSTRACTS OF JAPAN, vol. 7, no. 238 (P-231)(1383), 22nd October 1983; & JP-A-58 126 502 (NIHON ITA GLASS K.K.) 28-07-1983**

Remarks:
The file contains technical information submitted after the application was filed and not included in this specification

EP 0 193 269 B2

Description

[0001] The present invention relates to processes for preparing articles such as optical devices, bearing silica coatings thereon.

[0002] Improvement in the transmittance of light through optical devices such as windows, solar collector cover plates, lenses and prisms has long been sought so as to increase their usefulness. Optical devices having surfaces coated with antireflecting layers, typically having an optical thickness of one quarter of a wavelength, are known. Also known are optical devices in which surface reflections are reduced by altering the surface to provide a gradient index of refraction between that of the medium traversed by the incident light, such as air and that of the body of the optical device.

[0003] One method for providing such an altered surface is disclosed in Great Britain Patent No. 29,561. It involves tarnishing glass surfaces in aqueous solutions of sulphuretted hydrogen in order to reduce the reflection of light therefrom. Such a method is not useful for producing an antireflection surface on polymeric substrates.

[0004] Another method for providing such an altered surface is disclosed in Nicoll (U.S. Patent No. 2,445,238). This patent discloses a method for reducing reflection from glass surfaces in which the glass is heated in a vapor of hydrofluoric acid to form a skeletonized surface. Such skeletonized surfaces are difficult to reproduce and maintain.

[0005] Moulton (U.S. Patent No. 2,432,484) discloses a technique for forming a non-gelling, nonuniformly dispersed layer of anhydrous colloidal particles on the surface of articles. The particles form a random arrangement of peaks on the article surface to provide antireflection characteristics.

[0006] Moulton (U.S. Patent Nos. 2,536,764 and 2,601,123) discloses a transparent binder coating prepared using a dilute solution of tetraethylorthosilicate in organic solvent to render the colloidal particulate layer taught in the '484 patent resistant to wiping and handling, as such layers are inherently readily susceptable to injury.

[0007] Geffcken et al. (U.S. Patent No. 2,366,516) disclose an antireflection layer formed by applying an aqueous dispersion of a gel-like low-hydrated oxide, such as silicon dioxide, to an object and heating the coated object to a temperature of 250°C to form a hardened layer. Such a layer cannot be applied to most polymer substrates due to degradation of the substrate by heating to 250°C.

[0008] Baker et al. (U.S. Patent No. 3,301,701) disclose rendering a glass base antireflective by coating with a finely divided silica substantially free of silica gel. Such a coating would be expected to be brittle, weak, and powdery.

[0009] Land et al. (U.S. Patent No. 3,833,368) disclose antireflection coatings for photographic products which are an eighth-wave layer of a fluorinated polymer applied over an eighth-wave layer of silica, the silica layer having been formed from an aqueous colloidal silica sol.

[0010] Swerdlow (U.S. Patent No. 4,409,285) discloses an antireflection coating for optical surfaces, the coating formed from silica and or alumina particles in a polymeric binder with particles protruding from the surface of the binder. 20 to 98 weight percent of the particles have a size in the range of 7 to 50 nanometers (nm) and 5 to 65 weight percent of the particles have a size in the range of 75 to 150 nm.

[0011] Yoldas (U.S. Patent Nos. 4,271,210 and 4,346,131) and McCollister et al. (U.S. Patent No. 4,273,826) disclose anti-reflection coatings produced by coating a substrate with a metalio-organic compound, e.g. alkoxide, and heating the coated substrate at temperatures which decompose the organic components of the coating leaving a metal oxide layer on the substrate. The temperatures necessary to decompose the organic components would also decompose polymeric substrates.

[0012] Dorer et al. (U.S. Patent No. 4.190.321) disclose an antireflective coating of a metal oxide in the form of discrete leaflets of varying heights and shapes. This coating is susceptible to damage during handling due to the fragility of the leaflet structure.

[0013] Cathro et al, (Silica Low-Reflection Coatings for Collector Covers, by a Dip-Coating Process, SOLAR ENERGY, Vol. 32, No. 5, 1984, pp. 573-579) disclose low-reflection silica coatings prepared from ethanol-based silica sols which are aged at pH 7. Aging causes an increase in optical density and viscosity due to the agglomeration of silica particles prior to coating. Although good adhesion of the coating to glass is said to be obtained by heating at elevated temperatures, adhesion to polymeric substrates is poor, i.e., the coating can be wiped from the surface of the substrate by rubbing with a tissue.

Summary of the Invention

[0014] The present invention is directed to a process for forming a coated article comprising coating a polymeric substrate with a solution containing 0.2 to 15 weight percent colloidal silica particles having an average primary particle size of less than 20 nm (200A), and drying said coating at a temperature of less than 200° C to form a polymeric substrate having a coating of a continuous gelled network of silica particles which is transparent, provides a substantially smooth surface, is substantially uniform in thickness and is substantially permanently adhered to said polymeric substrate providing a 180° peelback value of at least 500 g/cm.

[0015] The coating adheres very well to polymeric substrates and can provide such substrates with excellent average reduction in specular reflectance, e.g., at least two percent. When the polymeric substrate is transparent, the coating can provide an average increase in transmission therethrough of normal incident light in the wavelength range of 400 to 800 nm over the transmission through an uncoated substrate of the same material. The increase in transmission is preferably at least two percent and up to as much as ten percent or more. The coating can also provide antistatic properties and reduced surface resistivity to polymeric film and sheet materials, subject to static build-up. The coating also preferably provides abrasion resistance and slip properties to polymeric materials, such as film and sheet materials, thereby improving their handleability.

Brief Description of the Drawings

[0016]

Fig. 1 is a transmission electron micrograph of a cross section of an article of the invention;
Fig. 2 is a plot of a curve 2 of the percentage of light reflected from an uncoated polyethylene terephthalate film substrate and of a curve 3 of a coated polyethylene terephthalate film substrate according to the invention; and
Fig. 3 is a plot of a curve 4 of the percentage of light transmitted through an uncoated polyethylene terephthalate film substrate and of a curve 5 of a coated polyethylene terephthalate film substrate according to the invention.

Detailed Description of the Invention

[0017] The article obtained with the process of the invention is a polymeric substrate bearing a continuous gelled network of silica particles. The particles have an average primary particle size of less than 20 nm (200 A). As used herein, the term "continuous" refers to covering the surface of the substrate with virtually no discontinuities or gaps in the areas where the gelled network is applied. The term "geiled network" refers to an aggregation of colloidal particles linked together to form a porous three-dimensional network. The term "porous" refers to the presence of voids between the silica particles. The term "primary particle size" refers to the average size of unagglomerated single particles of silica.

[0018] The articles comprise a polymeric substrate which may be of virtually any construction, transparent to opaque, having a flat, curved, or complex shape and have formed thereon a continuous gelled network of silica particles. When the coating is applied to transparent polymeric substrates to achieve increased light transmissivity, the coated article preferably exhibits a total average increase in transmissivity of normal incident light of at least two percent and up to as much as ten percent or more, depending on the substrate coated, over a range of wavelengths extending at least between 400 to 800 nm. An increase in transmissivity can also be seen at wavelengths into the infrared portion of the spectrum.

[0019] The polymeric substrates may comprise polymeric sheet, film, or molded material such as polyester, polyimide, polystyrene, polymethylmethacrylate, polycarbonate, polysulfone, polyacrylate, and cellulose acetate butyrate.

[0020] Figure 1, a transmission electron micrograph of a coating 1 useful in the invention at a magnification of 300.000X, shows that the coating is continuous, i.e., covers the surface of the substrate with virtually no discontinuities or gaps, and provides a substantially smooth surface which has only minor surface imperfections. Fig. 1 further shows that the coating 1 is substantially uniform in thickness.

[0021] The coating is substantially permanently adhered to polymeric substrates to which it is applied, i.e., it provides a 180° peelback value of at least about 500 g/cm when tested according to a modification of ASTM Test Method D3330, generally with failure at the adhesive layer and no coating removal from the substrate. In the modified lest method, a 1.9 cm wide strip of Scotch Brand Magic transparent tape, available from 3M Company, is adhered to the test sample by rolling a 2 kg roller back and forth twice across the tape. The tape is then peeled from the test sample at 180° at a rate of 2 cm/min.

[0022] The excellent adhesion of the coating to the polymeric substrate and the adhesive of the test tape also demonstrates the utility of the coating as a primer for adhering adhesives to polymeric substrates, e.g, polyester films.

[0023] The gelled network provides a porous coating having voids between the silica particles. If the open porosity is too small, the properties of the coating, such as adhesion and antireflectance may be reduced. If the open porosity is too large, the coating is weakened and may have reduced adhesion to the polymeric substrate. Generally, the colloidal solution from which the gelled network is obtained is capable of providing an open porosity of 25 to 70 percent, preferably 30 to 60 percent when dried. The open porosity is determined by drying a sufficient amount of the colloidal solution to provide a dried product sample of about 50 to 100 mg and analyzing the sample using a "Quantasorb" surface area analyzer available from Quantachrome Corp., Syosett, NY.

[0024] The voids of the porous coating provide a multiplicity of subwavelength interstices where the index of refraction abruptly changes from that of air to that of the coating material. These subwavelength interstices which are present throughout the coating layer, provide a coating which may have a calculated index of refraction of from 1.15 to 1.40,

preferably 1.20 to 1.30 depending on the porosity of the coating. When the porosity of the coating is high, e.g., about 70 percent, lower values for the index of refraction are obtained. When the porosity of the coating is low, e.g., 25 percent, higher values for the index of refraction are obtained. The index of refraction of the coating is dependent on the relative volume ratios of the particles and the interstices and the index of refraction of the silica, i.e., 1.47. For purposes of this invention, the index of refraction (RI) is calculated using the formula:

$$RI = \frac{Po}{100} + \left(\frac{100-Pc}{100}\right)1.47$$

where Po is the value of the open porosity.

[0025] The average primary particle size of the colloidal silica particles is less than 20 nm (200 A) to achieve good adhesion of the coating to the substrate. The average primary particle size of the colloidal silica particles is more preferably less than about 7nm (70 A) when antireflection properties are sought. When the average particle size becomes too large, the resulting dried coating surface is less efficient as an antireflection coating.

[0026] The dried coating is preferably from about 20 to 500 nm thick. Such coatings provide good adhesion and antistatic properties. When the coating thickness is too great, the coating has reduced adhesion and flexibility and may flake off or form powder under mechanical stress. When antireflection properties are sought, the dried coating thickness is preferably about 70 to 250 nm, more preferably 100 to 200 nm.

[0027] Articles such as transparent sheet or film materials may be coated on a single side or on both sides to increase transmissivity, the greatest increase being achieved by coating both sides.

[0028] The process of the invention comprises coating a polymeric substrate with a solution containing about 0.2 to 15 weight percent colloidal silica particles having an average primary particle size less than 20 nm (200 A). Preferably less than about 7 nm (70 A). and drying the coating at a temperature less than 200°C. preferably in the range of 80 to 120°C.

[0029] Coating may be carried out by standard coating techniques such as bar coating, roll coating, curtain coating, rotogravure coating, spraying and dipping. The polymeric substrate may be treated prior to coating to obtain a uniform coating. Various known treatment techniques include corona discharge, flame treatment, and electron beam. Generally, no pretreatment is required.

[0030] The colloidal silica solution, e.g., a hydrosol or organosol, is applied to the polymeric substrate of the article to be coated and dried at a temperature, less than about 200°C, preferably 80-120°C to remove water or organic diluents. The coating may also be dried at room temperature, provided the drying time is sufficient to permit the coating to dry completely. The drying temperature should be less than that at which the substrate degrades. The resulting hygroscopic coating is capable of absorbing and/or rehydrating water in an amount of up to about 15 to 20 weight percent, depending on ambient temperature and humidity conditions.

[0031] The colloidal silica solution, finely divided solid silica particles of ultramicroscopic size in a liquid, utilized in the present invention, may be acid stabilized, sodium stabilized, or ammonia stabilized. It is generally helpful to acidify sodium stabilized silica sols to a pH of 3.5 to 4.0, e.g., with glacial acetic acid, to prevent particle agglomeration prior to preparation of the coating solution when alcohol is used as a diluent. Examples of commercially available colloidal silicas useful in the invention include Nalco 2326 and Nalco 1034A, available from Nalco Chemical Co., and Ludox LS, available from E. I. duPont de Nemours Co., Inc.

[0032] The colloidal coating solution should contain 0.2 to 15 weight percent, preferably about 0.5 to 6 weight percent, colloidal silica particles. At particle concentrations above 15 weight percent, the resulting coating may have reduced uniformity and exhibit reduced adhesion to the polymeric substrate surface. Difficulties in obtaining a sufficiently thin coating to achieve increased light transmissivity and reduced reflection may also be encountered at concentrations above 15 weight percent. At concentrations below 0.2 weight percent, process inefficiencies result due to the large amount of solvent which must be removed and antireflection properties may be reduced.

[0033] The thickness of the applied wet coating solution is dependent on the concentration of silica particles in the coating solution and the desired thickness of the dried coating. The thickness of the wet coating solution is preferably such that the resulting dried coating thickness is from 20 to 500 nm thick.

[0034] The coating solution may also optionally contain a surfactant to improve wettability of the solution on the polymeric substrate, but inclusion of an excessive amount of surfactant may reduce the adhesion properties of the coating. Examples of suitable surfactants include Tergitol TMN-6 (Union Carbide Corp.) and Triton X-100 (Rohm and Haas Co.). Generally, the surfactant can be used in amounts of up to about 0.5 weight percent of the solution.

[0035] The coating ingredients may optionally contain a polymeric binder. Useful polymeric binders include polyvinyl alcohol, polyvinyl acetate, polyesters, polyamides, polyvinyl pyrrolidone, copolyesters, copolymers of acrylic acid and/

or methacrylic acid, and copolymers of styrene. The coating solution can contain up to about 50 weight percent of the polymeric binder based on the weight of the silica particles. Useful amounts of polymeric binder are generally in the range of 0.5 to 10.0 weight percent.

[0036] Addition of various adjuvants, such as slip agents and processing oils, to the substrate material may reduce the adhesion of the coating to the polymeric substrate.

[0037] The following specific, examples will serve to illustrate the invention. In these examples, all percentages and parts are by weight unless otherwise indicated.

Example 1

[0038] Six grams of Nalco 2326 (ammonia stabilized colloidal silica; 14.5% colloidal silica as SiO_2; particle size 5 nm (50 A): available form Nalco Chemical Company) was added to 100 g ethanol to provide a very clear coating solution. A 0.1 mm biaxially oriented polyethylene terephthalate film containing an ultraviolet absorber was dipped in the coating solution, air dryed, and dried at 100°C for two minutes. The resulting coating was porous, continuous, and similar to the coating shown in Fig. 1 in appearance. The coating thickness was about 120 nm.

[0039] The coating adhered aggressively to the substrate. A 1.9 cm (3/4 inch) wide strip of Scotch Brand Magic transparent tape was applied to coated and uncoated film samples by hand pressure. A force of about 180 g/cm tape width was required to remove the tape from the uncoated sample, while a force of about 530 g/cm tape width was required to remove the tape from the coated sample, demonstrating a remarkable increase in the adhesion of the tape. The adhesive of the tape did not remove the coating from the coated film, but exhibited adhesive split of the adhesive layer leaving adhesive residue on the coating further demonstrating the strong bond of the adhesive to the coated film. No adhesive split was observed when the tape was removed from the uncoated sample.

[0040] The antireflection and transmission properties of the film were measured using an IBM UV-VIS 9432 Spectrophotometer at wavelengths of from 350 to 800 nm. An uncoated sample of the film was also measured for comparative purposes. The results of these tests are shown in Figs. 2 and 3. As can be seen from Fig. 2. the reflectance of the uncoated sample. curve 2, was 12% at 600 nm, while the reflectance of the coated sample, curve 3, was about 2% at 600 nm. As can be seen from Fig. 3, the light transmission of the uncoated film, curve 4, was about 88% at 600 nm, while the light transmission of the coated sample, curve 5, was about 98% at 600 nm. This demonstrates the excellent reduction of reflectance and increase in transmission of light provided by the coating.

Example 2

[0041] A coating solution was prepared by diluting colloidal silica (Nalco 2326) with ethanol to a concentration of 2.5% solids and adding 0.01% Tergitol TMN-6. The solution was coated on 0.1 mm thick polyethylene terephthalate film using a rotogravure coating roll. The coated film was dried at 93°C for three minutes. The resulting coating was porous, continuous, and about 100 nm thick. The coating was substantially similar to the coating shown in Fig. 1. The dried coating was observed to have good antireflection properties.

[0042] Samples of the coated film as well as samples of uncoated film were tested for adhesion using the modified ASTM Test Method D3330 described hereinabove. The uncoated film had an adhesion value of 189 g/cm tape width with no adhesive split from the tape. The coated sample had an adhesion value of 559 g/cm tape width. The tape did not remove the coating from the film, but exhibited adhesive split of the adhesive layer, again demonstrating the excellent adhesion of the coating to the substrate and the excellent adhesion of the adhesive to the coating.

Examples 3-15

[0043] Various transparent polymeric sheet materials, as identified in Table 1, were coated by dipping the materials in a coating solution containing 1.5% colloidal silica (Nalco 2326) or by wiping the solution on each side of the sheet material with a tissue-wrapped glass rod and drying the coated sample.

Table 1

Material	Type	Thickness (mm)
A	polymethylmethacrylate (Rohm and Haas Co.)	0.67
B	polycarbonate (CR-39, PPG Inc.)	3.12
C	polycarbonate (Lexan, General Electric Co.)	1.94
D	cellulose acetate butyrate	2.15

[0044] The following coating solutions were used to coat the various sheet materials:

Solution I	
ethanol	135 g
Nalco 2326 silica sol	15 g
Tergitol TMN-6	0.15 g

Solution II	
water	135 g
Nalco 2326 silica sol	15 g
Tergitol TMN-6	0.3 g

[0045] For each example, the substrate material, coating method, coating solution, and drying temperature, together with the resulting light transmission determined using an IBM UV-VIS 9432 Spectrophotometer at wavelengths of from 400 to 800 nm, are set forth in Table 2. Light transmission data for uncoated materials are also set forth in Table 2 for comparative purposes.

Table 2

Example	Material	Coating Method	Coating Solution	Drying Temp. (°C)	% Transmission at wavelengths (nm) 400	500	600	700	800	Average percent increase in transmission
3 (Comp)*	A	none	---	---	92.0	92.5	92.5	92.5	92.5	---
4	A	dip	I	80	91.5	93.5	94.5	95.5	95.5	2.0
5	A	wipe	I	80	96.5	94.8	94.7	95.3	95.6	3.2
6 (Comp)	B	none	---	---	88.5	90.5	91.0	91.4	91.8	---
7	B	wipe	II	22	96.0	97.5	97.5	97.0	96.0	6.8
8	B	wipe	II	80	92.1	94.2	96.0	97.1	97.5	5.2
9	B	wipe	I	22	93.0	96.0	97.4	97.9	97.5	6.3
10	B	wipe	I	80	91.8	94.5	97.0	98.0	98.2	5.8
11 (Comp)	C	none	---	---	91.7	92.0	92.0	92.1	92.1	---
12	C	wipe	I	80	94.1	92.6	94.1	96.2	98.0	3.3
13 (Comp)	D	none	---	---	83.6	87.9	87.5	90.1	90.2	---
14	D	dip	II	22	87.1	93.8	93.7	96.2	96.1	6.3
15	D	wipe	I	80	86.0	90.4	89.1	91.8	92.8	2.5

*"Comp" denotes comparative examples.

[0046] As can be seen from the data in Table 2, the coatings provide an excellent increase in light transmission for each of the materials which were coated. Each coated sample exhibited at least two percent average increase in light transmission. The greatest increase in transmission was achieved on the CR-39 polycarbonate with the average per-

cent increase in transmission for Example 7 being 6.8 percent.

Claims

1. A process for forming a coated article comprising coating a polymeric substrate with a solution containing 0.2 to 15 weight percent colloidal silica particles having an average primary particle size of less than 20 nm (200A), and drying said coating at a temperature of less than 200 °C to form a polymeric substrate having a coating of a continuous gelled network of silica particles which is transparent, provides a substantially smooth surface, is substantially uniform in thickness and is substantially permanently adhered to said polymeric substrate providing a 180° peelback value of at least 500 g/cm.

2. The process of claim 1 wherein the coating is dried at a temperature in the range of 80°C to 120 °C.

3. The process of any preceding claim wherein said coating is 20 to 500 nm thick.

4. The process of any preceding claim wherein said coating is prepared from a colloidal solution capable of providing a dried product having an open porosity of between 25 and 70 percent.

5. The process of any preceding claim wherein said coating contains up to about 20 weight percent water.

6. The process of any preceding claim wherein said substrate is transparent.

7. The process of claim 6 wherein the transmission therethrough of normal incident light in the wavelength range of 400 to 800 nm is increased over the transmission through an uncoated substrate of the same compositions.

8. The process of claim 7 wherein said average transmission is increased at least 2 percent.

9. The process of either of claims 7 and 8 wherein said coating is from about 70 to 250 nm thick.

10. The process of any preceding claim wherein said coating has an index of refraction of between 1.15 and 1.40.

Patentansprüche

1. Verfahren zur Erzeugung eines beschichteten Gegenstands, umfassend Beschichten eines polymeren Substrats mit einer Lösung, die 0,2 bis 15 Gewichtsprozent kolloidale Silicateilchen mit einer mittleren Primärteilchengröße von weniger als 20 nm (200 Å) enthält, und Trocknen der Beschichtung bei einer Temperatur von weniger als 200 °C, um ein polymeres Substrat mit einer Beschichtung eines zusammenhängenden, durch Gelbildung erstarrten Netzwerks von Silicateilchen zu erzeugen, die transparent ist, eine im wesentlichen glatte Oberfläche schafft, eine im wesentlichen gleichförmige Dicke aufweist und im wesentlichen dauerhaft auf dem polymeren Substrat haftet und einen 180°-Ablösewert von mindestens 500 g/cm gewährt.

2. Verfahren nach Anspruch 1, bei welchem die Beschichtung bei einer Temperatur im Bereich von 80 °C bis 120 °C getrocknet wird.

3. Verfahren nach einem der vorstehenden Ansprüche, bei welchem die Beschichtung 20 bis 500 nm dick ist.

4. Verfahren nach einem der vorstehenden Ansprüche, bei welchem die Beschichtung aus einer kolloidalen Lösung hergestellt wird, mit der ein getrocknetes Produkt mit einer offenen Porosität zwischen 25 und 70 Prozent geschaffen werden kann.

5. Verfahren nach einem der vorstehenden Ansprüche, bei welchem die Beschichtung bis zu etwa 20 Gewichtsprozent Wasser enthält.

6. Verfahren nach einem der vorstehenden Ansprüche, bei welchem das Substrat transparent ist.

7. Verfahren nach Anspruch 6, bei welchem die Durchlässigkeit bei senkrecht einfallendem Licht im Wellenlängen-

bereich zwischen 400 und 800 nm gegenüber der Durchlässigkeit durch ein unbeschichtetes Substrat der gleichen Zusammensetzungen erhöht ist.

8. Verfahren nach Anspruch 7, bei welchem die mittlere Durchlässigkeit um mindestens 2 Prozent erhöht ist.

9. Verfahren nach Anspruch 7 oder 8, bei welchem die Beschichtung zwischen etwa 70 und 250 nm dick ist.

10. Verfahren nach einem der vorstehenden Ansprüche, bei welchem die Beschichtung einen Brechungsindex zwischen 1,15 und 1,40 hat.

Revendications

1. Procédé de formation d'un article revêtu comprenant l'application en couche sur un substrat polymère d'une solution contenant 0,2 à 15 % en poids de particules de silice colloïdale, ayant une taille primaire moyenne des particules de moins de 20 nm (200 A), et le séchage dudit revêtement à une température inférieure à 200°C pour former un substrat polymère comportant un revêtement d'un réseau gélifié continu de particules de silice, qui est transparent, donne une surface essentiellement lisse, est d'une épaisseur pratiquement uniforme et est amené à adhérer de manière pratiquement permanente audit substrat polymère, en donnant une valeur de pelage à 180° d'au moins 500 g/cm.

2. Procédé suivant la revendication 1, dans lequel le revêtement est séché à une température de l'ordre de 80 à 120°C.

3. Procédé suivant l'une quelconque des revendications précédentes, dans lequel ledit revêtement a une épaisseur de 20 à 500 nm.

4. Procédé suivant l'une quelconque des revendications précédentes, dans lequel ledit revêtement est préparé à partir d'une solution colloïdale capable de donner un produit séché ayant une porosité ouverte comprise entre 25 et 70 %.

5. Procédé suivant l'une quelconque des revendications précédentes, dans lequel ledit revêtement contient jusqu'à environ 20 % en poids d'eau.

6. Procédé suivant l'une quelconque des revendications précédentes, dans lequel ledit substrat est transparent.

7. Procédé suivant la revendication 6, dans lequel la transmission, à travers ce substrat, d'une lumière incidente normale dans l'intervalle de longueurs d'onde de 400 à 800 nm est accrue par rapport à la transmission à travers un substrat non revêtu, de la même composition.

8. Procédé suivant la revendication 7, dans lequel ladite transmission moyenne est augmentée d'au moins 2 %.

9. Procédé suivant la revendication 7 ou la revendication 8, dans lequel ledit revêtement est d'une épaisseur d'environ 70 à 250 nm.

10. Procédé suivant l'une quelconque des revendications précédentes, dans lequel ledit revêtement a un indice de réfraction compris entre 1,15 et 1,40.

FIG.1

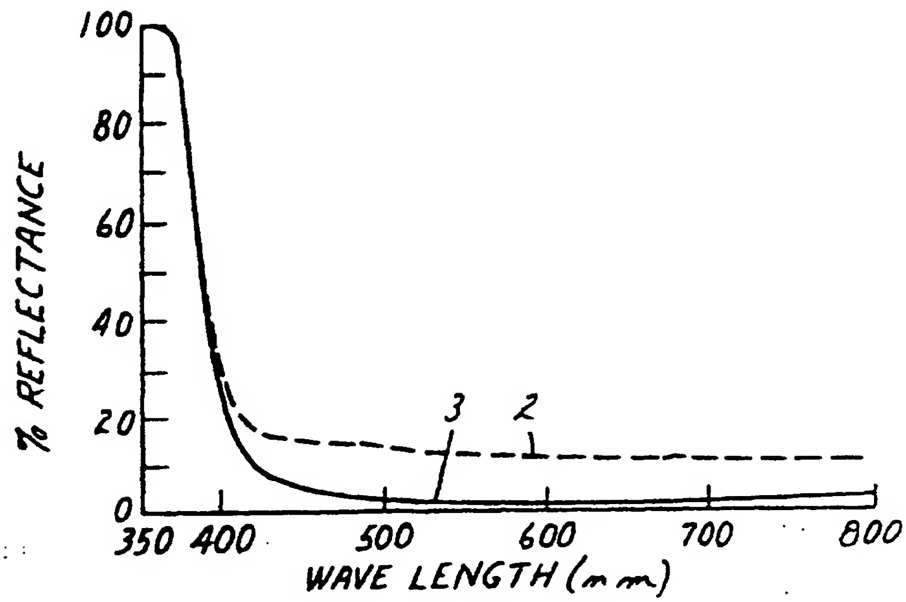
100
80
60
40
20
0
% REFLECTANCE
3
2
350 400
500
600
700
800
WAVE LENGTH (nm)

FIG. 2

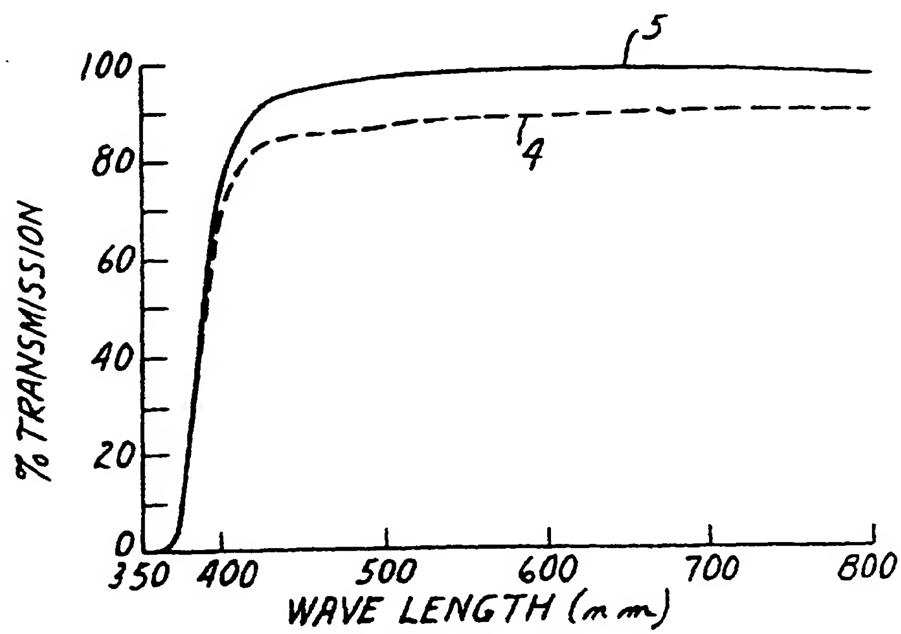
5
100
80
60
40
20
0
4
% TRANSMISSION
350 400
500
600
700
800
WAVE LENGTH (nm)

FIG. 3